Stabilizing Lithium Metal Anodes by Interfacial Layer and New Electrolytes

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PNNL

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Stanford University/SLAC National Laboratory

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Project ID bat365

Overview

Timeline

- Project start date: 10/01/2021
- Project end date: 9/30/2026
- Percent complete: 13 percent

Barriers

- Barriers addressed
  - Increasing the energy density of advanced lithium (Li) batteries beyond what can be achieved in today's Li-ion batteries is a grand scientific and technological challenge.

Budget

- Total project funding: DOE share $75M
- Funding received in FY 2022: $15M
- Funding for FY 2023: $15M

Partners

- Project lead: PNNL
- Team: Binghamton Univ., BNL, INL, GM, Penn State Univ., Stanford Univ./SLAC, Texas A&M, UC San Diego, Univ. of Maryland, Univ. of Pittsburgh, Univ. of Texas, Austin, Univ. of Washington
- Industry Advisory Board

Relevancy:

Project Objectives

- Develop next generation high-energy, low-cost batteries for electric vehicles

- Design, fabricate and validate high energy pouch cells up to 500 Wh kg^{-1}
- Scale up pouch cell capacity up to 5-10 Ah

- Demonstrate long cycle life of up to 1,000 deep charge-discharge cycles

- Achieve total control of battery chemistries for robust, scalable and commercially viable technologies

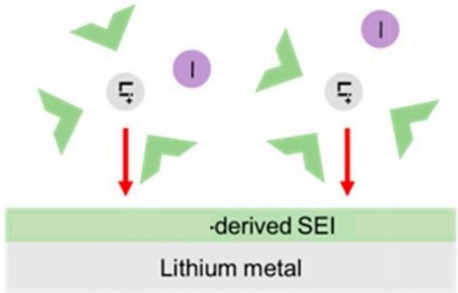
Approaches

- Fundamental breakthroughs in controlling the electrochemical reactions in high energy electrode materials and cells for next generation high-energy, low-cost batteries;
- Integrating development and discoveries from materials to cell level, and rapidly validating and incorporating latest results in realistic cells;
- Leveraging materials developed under other DOE programs, and state-of-the-art DOE facilities to understand and prevent degradation.
- Developing and deploying multi-disciplinary approaches and enhancing collaborations between national laboratories, universities and industry.

Technical approaches

Questions we want to answer (Bao):

1. How do we design high-CE electrolytes?
   - Solvation, ion conductivity, oxidative stability
2. How do we design coatings to mitigate the issues from electrolytes?
   - Reduce reaction from electrolyte, dissolution of SEI, uniform ion flux



Stanford/SLAC

Bulk
Ionic conductivity
Viscosity

Solvation
Solvation energy (Cui)
NMR
Raman
Simulation of solvation structure (Qin)

SEI
XPS, SEM
Cryo-EM (Cui)
QCM (Cui)

Electrochemical
Oxidative stability
Battery cycling
Transient CV (Cui)

Stanford/SLAC

Design

Synthesis

Battery 500

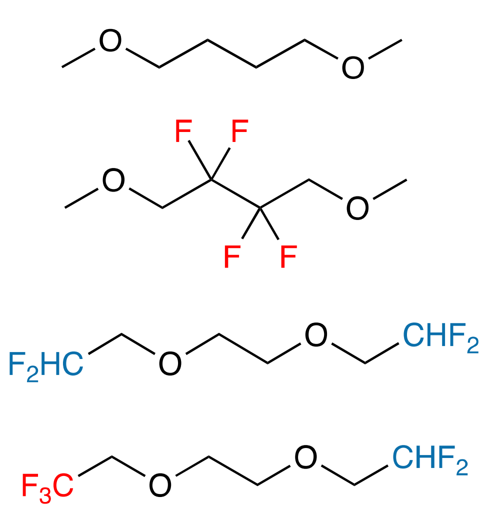
Validation, porch cell (PNNL)
High-V cathode (UT Austin)
SPAN (UCSD)
Thermal stability (Binghamton)
3D host (UW)

DOE US-German

Solid-state NMR
(FZ-Juelich)
SAXS (TUM)
QENS (TUM)
Transient EIS (ONL)

Battery 500 approaches towards high CE electrolytes

- Balancing solvation, oxidation stability and ionic transport



Bao, Cui, Qin

SLAC NATIONAL ACCELERATOR LABORATORY
STANFORD UNIVERSITY

- Functional additives

simultaneously stabilizing high-Ni cathode and Li anode

Gen 1: $LiPF_6$ in EC/DEC + FEC+ LiDFOB

Developing electrochemically inert co-solvent to achieve increased redox stability

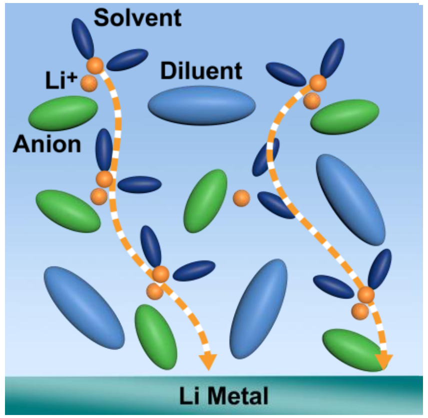
Gen 2: Gen 1 + new fluorinated co-solvent

Wang (PSU)

PennState

- Localized High concentration Electrolyte (LHCE) :

a. A base solvent (such as DME)
b. A Li salt (LiFSI) stable with Li
c. A diluent (such as TTE) with a very limited solvability of Li salt and fully mixable with base solvent.



Typical formula: LiFSI:1.2DME:3TTE

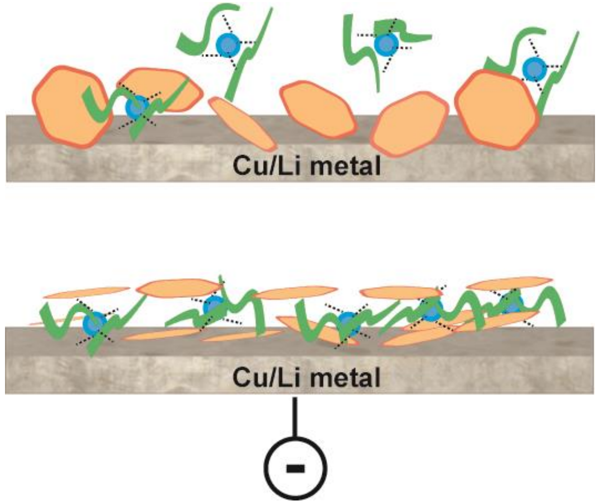
Zhang & Xu (PNNL)

Pacific Northwest NATIONAL LABORATORY

- Inorganic-SEI and electro-mechanic stabilization-stiffened electric double layer:

Gen 1: LiFSI-Py14FSI

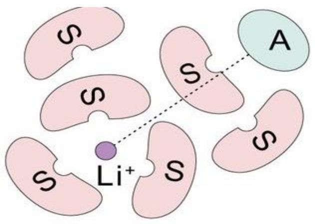
Gen 2 (typical formula): LiFSI-Py14FSI-M2FSI



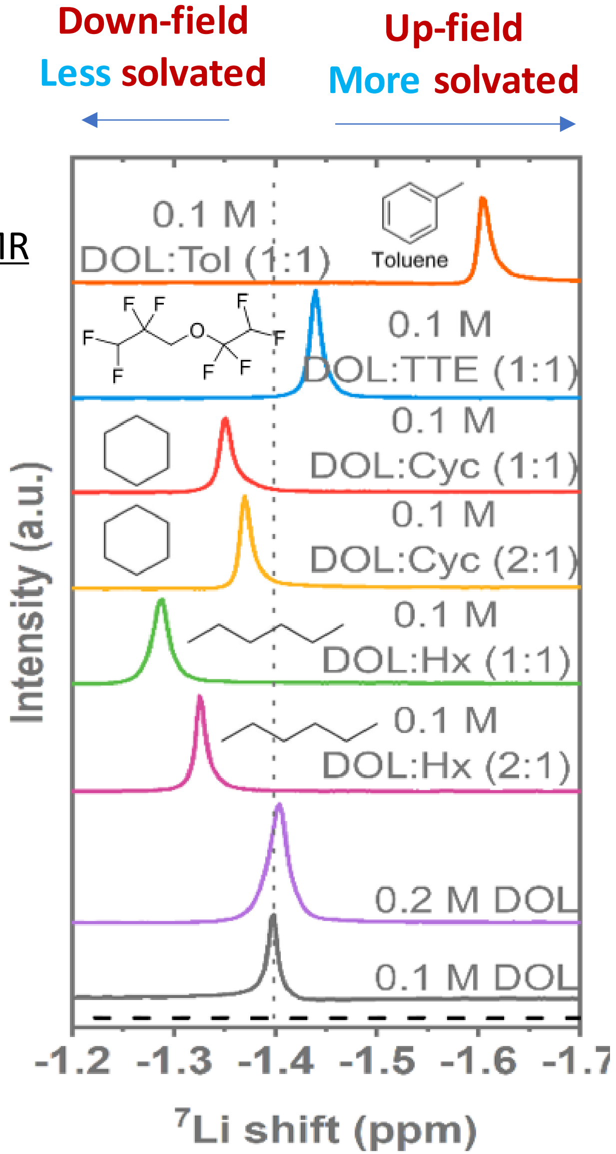
Wang (UMD)

UNIVERSITY OF MARYLAND

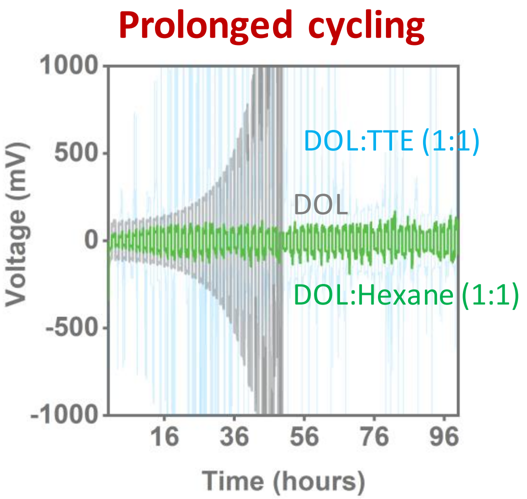
Technical accomplishments and progress: Less solvated Li^+, lower overpotential, more 2D Li deposition

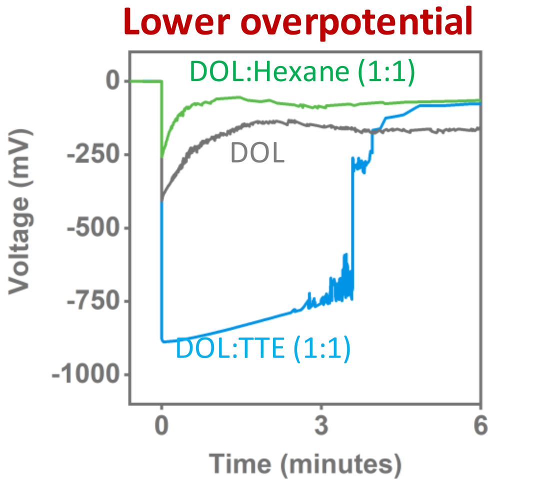


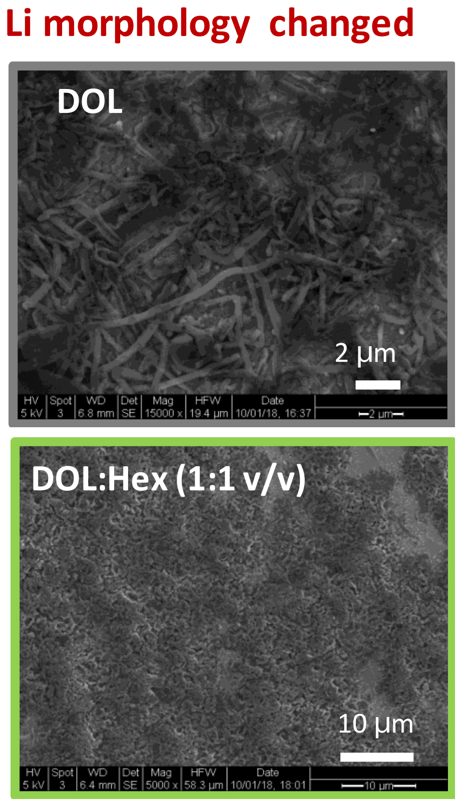
^{7}Li NMR



0.1M LiTFSI
Capillary NMR setup
100 µL sample in capillary
1M $LiClO_4$ in CD_3CN
deuterated solv.



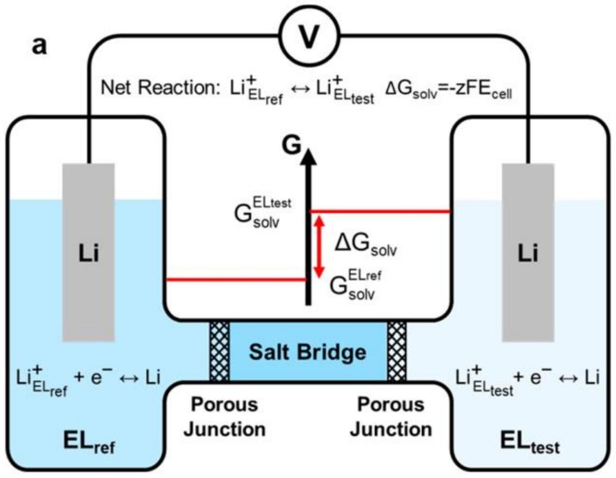




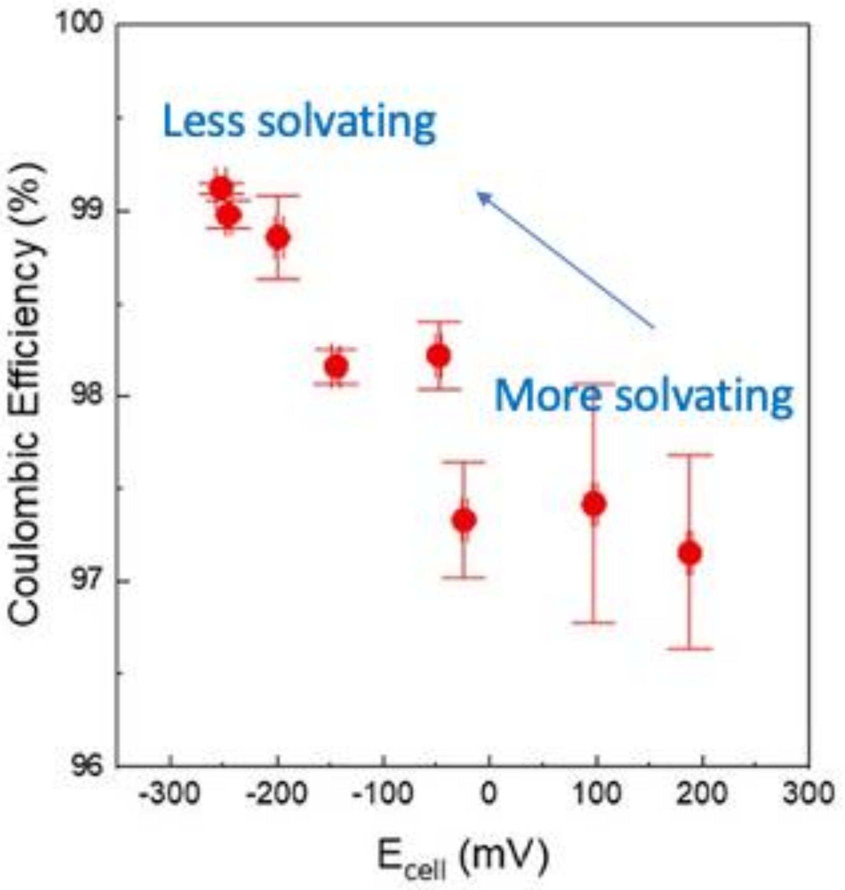
Li/Li
Current rate: 1 mA/cm^2
Capacity: 1 mAh/cm^2

C. V. Amanchukwu, J. Qin, Y. Cui, Z. Bao et al. **Adv. Energy Mater.**, 2019

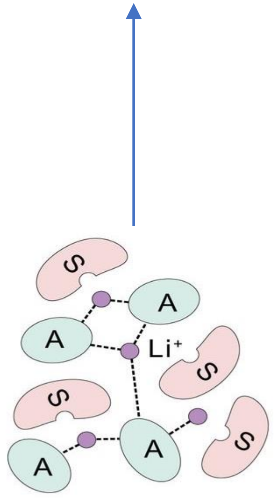
Technical accomplishments and progress: Lower solvation energy, more anion-derived SEI, higher CE



$\Delta G_{solv} = -zFE_{cell}$
z: number of electrons transferred
F: Faraday constant

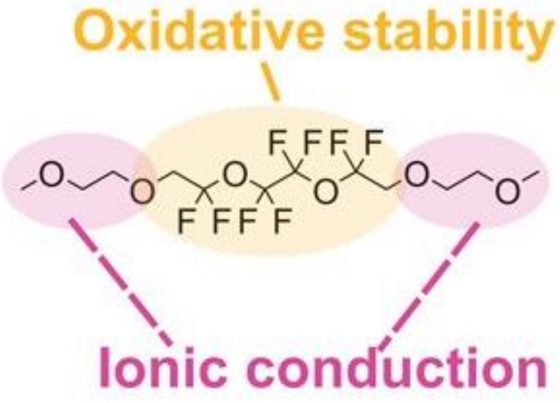


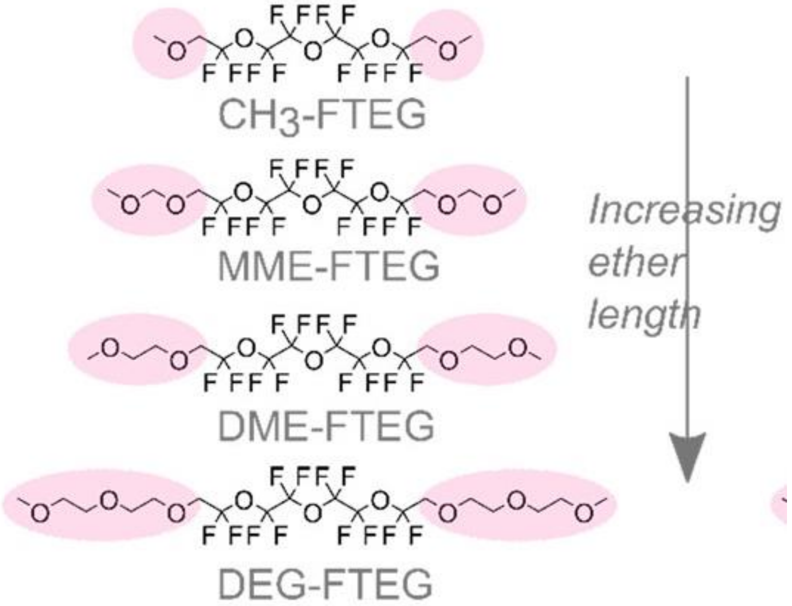
More anion-derived SEI



S.C. Kim, J. Qin, Z. Bao, Y. Cui et al., ***J. Am. Chem. Soc***. 2021, 143, 27, 10301−10308

Technical accomplishments and progress: Balancing ionic conductivity and oxidative stability





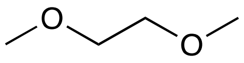
10^{-6} S/cm

10^{-3} S/cm

Higher ionic conductivity
Lower oxidative stability

C. V. Amanchukwu, Z. Yu, X. Kong, J. Qin, Y. Cui, Z. Bao, **J. Amer. Chem. Soc.**, 142, 7393-7403, 2020.

Technical accomplishments and progress: Rational design of weakly-solvating electrolyte solvents

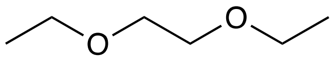


DME

- Solvation structures
- Oxidation stability
- Ionic conductivity

Goals:
high CE
High-V cathode
Safety, low cost

Steric effect

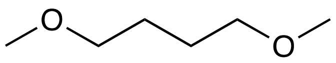


DEE

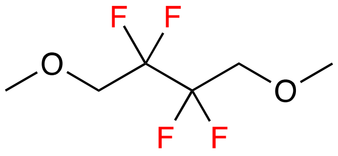
94 cycles

4 M LiFSI, DEE: Y. Chen, Z. Yu, Y. Cui, Z. Bao et al., **J. Am. Chem. Soc**. 2021, 143, 18703-18713.

Electronic effect



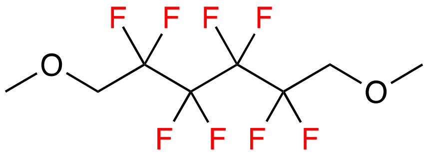
DMB



FDMB

90-110 cycles

1 M LiFSI, DMB, FDMB: Z. Yu, H. Wang, Y. Cui, Z. Bao et al., **Nature Energy**, 2020, 5, 526-533.

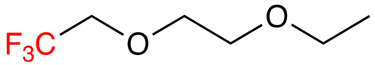


FDMH

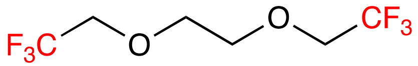
90 cycles

1 M LiFSI, DME-6FDMH: H. Wang, Z. Yu, Z. Bao, Y. Cui et al., **Adv. Mater.** 2021, 33, 2008619.

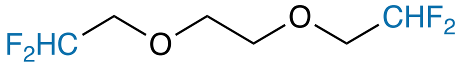
Fine tuning



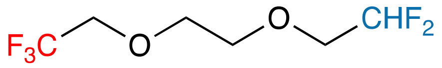
X3



X6



X4



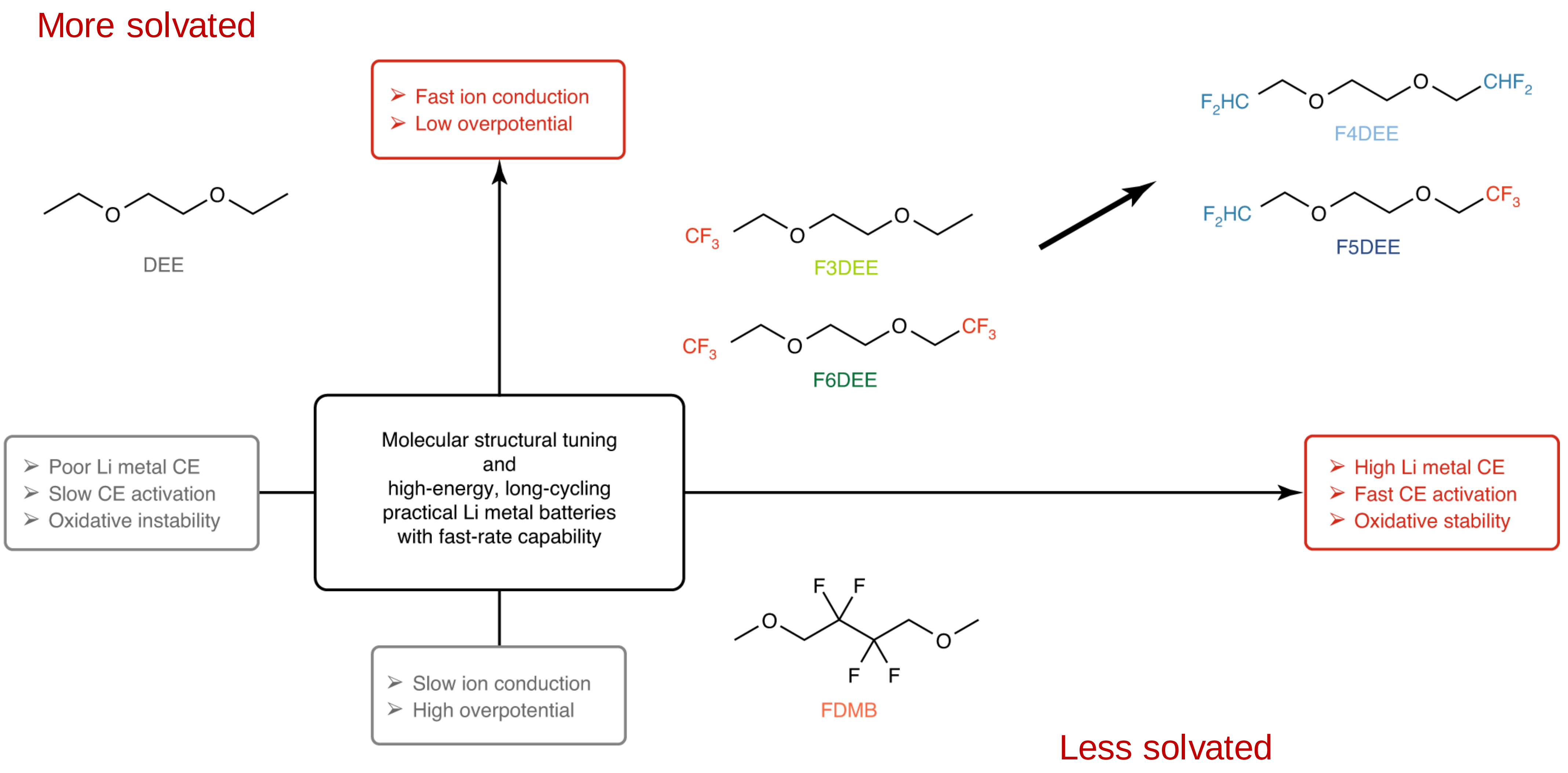
X5

1 M LiFSI, X-n: Z. Yu, Y. Cui, Z. Bao et al., **Nature Energy** 2022

200 cycles

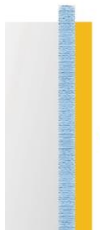
Testing conditions:
Thin-Li || high-loading NMC811 full-cell cycle life:
50-μm-thick-Li || 4.8 mAh/cm^2 NMC811, 2.8-4.4V, C/5 charge C/3 discharge, electrolyte 8 g/Ah

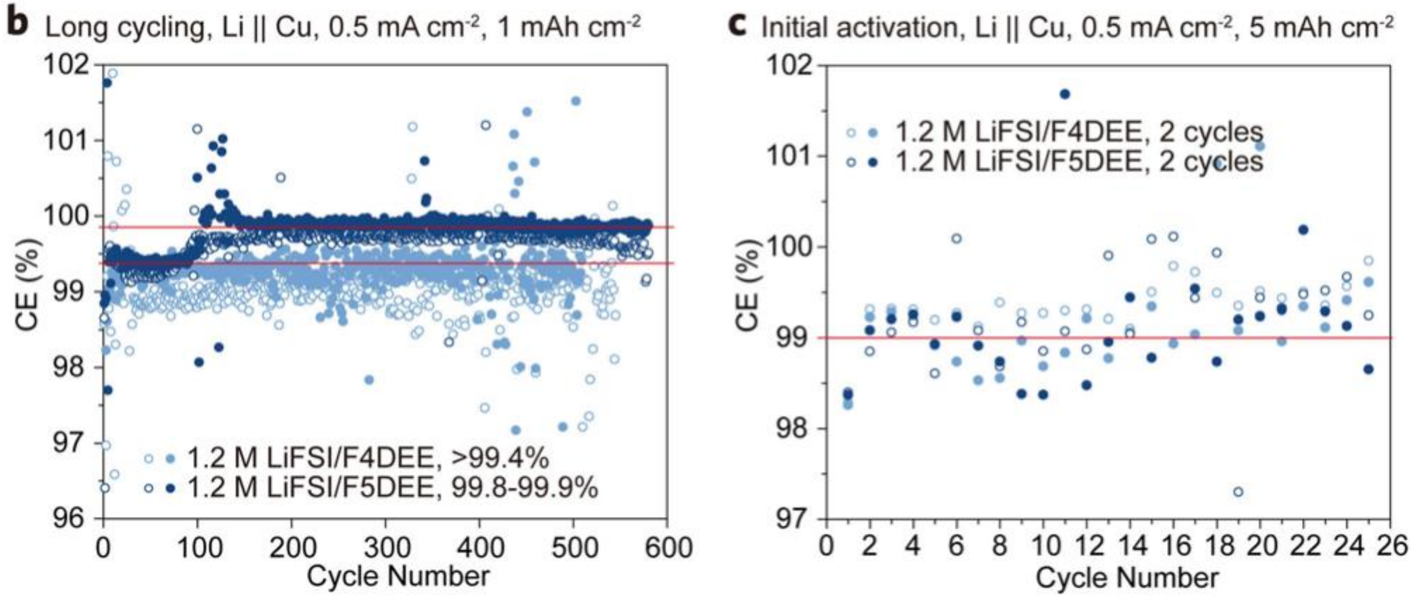
Technical accomplishments and progress: general findings on electrolyte design



Technical accomplishments and progress: our electrolyte has fast activation

Li/Cu half cell

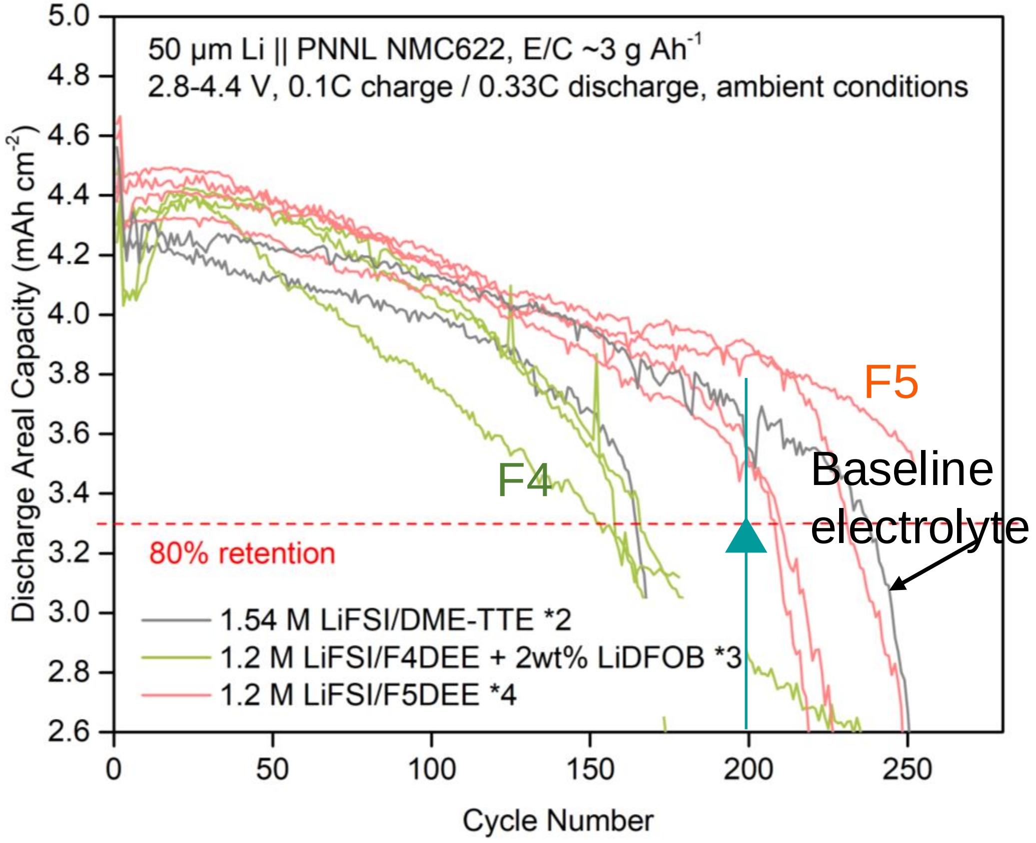




Fast activation:
FDMB CE>99%, in 5 cycles, average CE 99.5%
F4, F5, CE 99%, in 2 cycles, average CE 99.9%

- Battery500 cycling protocol (target: ▲)

(see Alt text)



Comparable or exceeding baseline electrolyte performance

Collaboration and Coordination with Other Institutions

PNNL: FDMB and X5 for pouch cells
Binghamton U. (Whittingham): thermal and oxidative stability
UT Austin (Manthiram): high-V and Co-free cathodes
UCSD (Liu): SPAN battery
UW (Yang): 3D host

Stanford/SLAC

Bulk
Ionic conductivity
Viscosity

Solvation
Solvation energy (Cui)
NMR
Raman
Simulation of solvation structure (Qin)

SEI
XPS, SEM
Cryo-EM (Cui)
QCM (Cui)

Electrochemical
Oxidative stability
Battery cycling
Transient CV (Cui)

Stanford/SLAC

Design

Synthesis

Battery 500

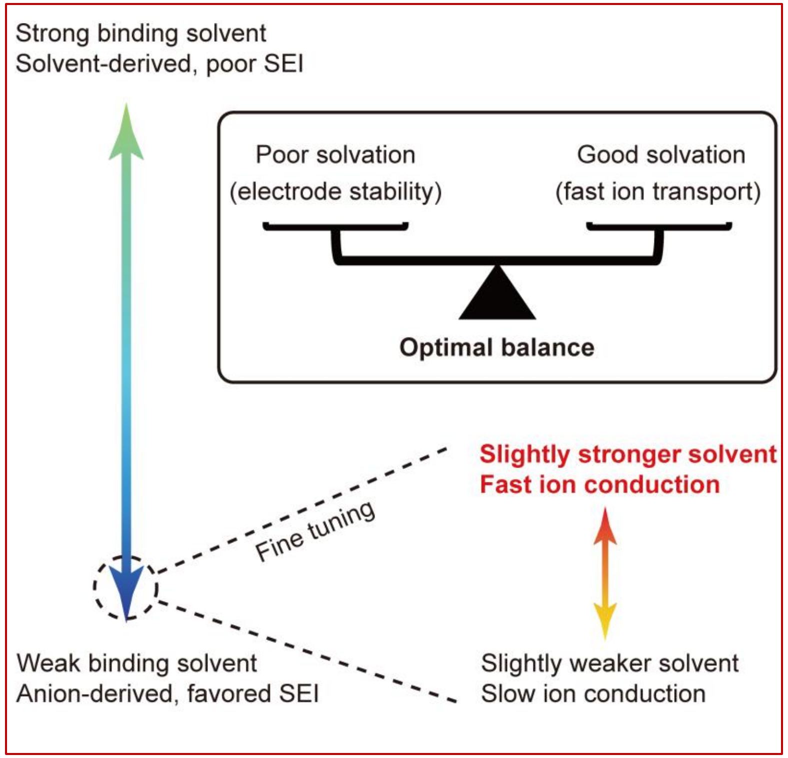
Validation, porch cell (PNNL)
High-V cathode (UT Austin)
SPAN (UCSD)
Thermal stability (Binghamton)
3D host (UW)

DOE US-German

Solid-state NMR
(FZ-Juelich)
SAXS (TUM)
QENS (TUM)
Transient EIS (ONL)

Proposed future research

- Understand the balance
- Causes for the initial lower CE
- Investigate higher current density failure mechanism and solutions
- Fine-tunning in different classes of solvent systems
- Combination of various systems
- Collaborate with other groups to further understand new electrolytes



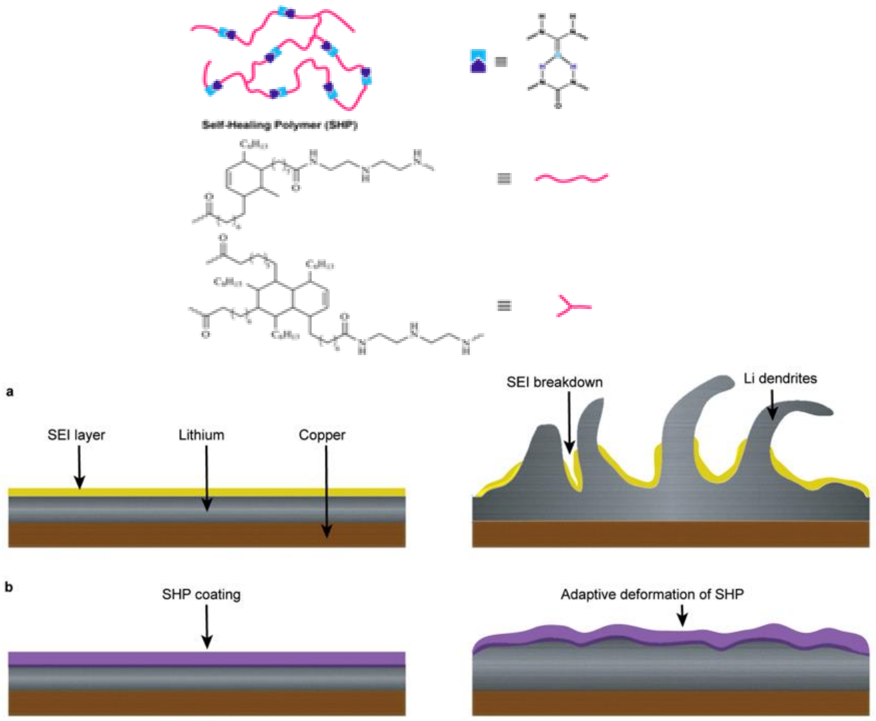
Summary

- We conducted a systematic study on the structure–performance relationships of new electrolytes via multiple theoretical and experimental tools.
- We found that crucial properties including Li^+–solvent coordination, solvation structure and battery performance.
- Our work emphasizes the critical yet less-studied direction, fast ion conduction, in the Li metal battery electrolyte research. It is critical to achieve a balance between fast ion conduction and electrode stability through fine-tuning the solvation ability of the solvent, and molecular design and synthetic tools play important roles.
- We believe that rational molecular-level design and chemical synthesis can endow the electrolyte field with more opportunities in the future.
- Collaborate with other groups to further understand new electrolytes are underway.

Technical Backup Slides

Technical accomplishments and progress: summary of work related to rational design of Li metal coatings

A flowable artificial SEI for Li metal

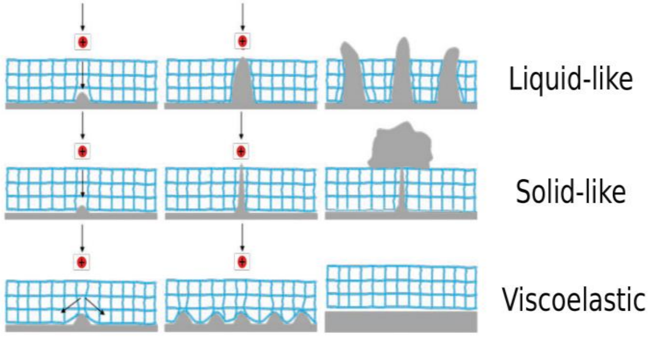


G. Zheng+, C. Wang+, A. Pei+, J. Lopez+, Y. Cui, Z. Bao et al. **ACS Energy Lett**. 1247–1255 (2016)

J. Lopez, Y. Cui, Z. Bao et al, **JACS** 2018

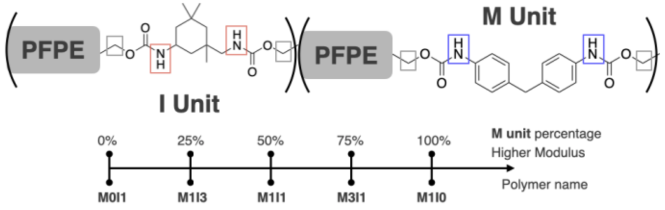
Effect of coating mechanics

Theoretical investigation



X. Kong, P. Rudnicki, S. Choudhury, Z. Bao, J. Qin, **Adv. Funct. Mater**. 2020, 1910138.

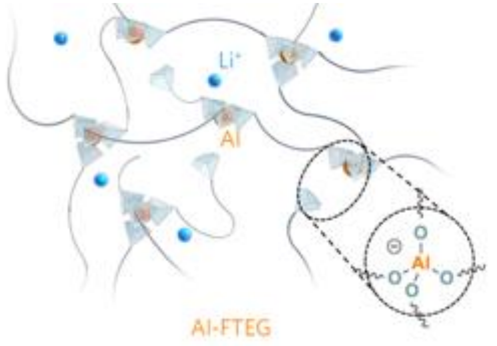
Experimental investigation



Z Huang, S Choudhury, N Paul, R Gilles, Z Bao, **Adv. Energy Mater.** (2021)

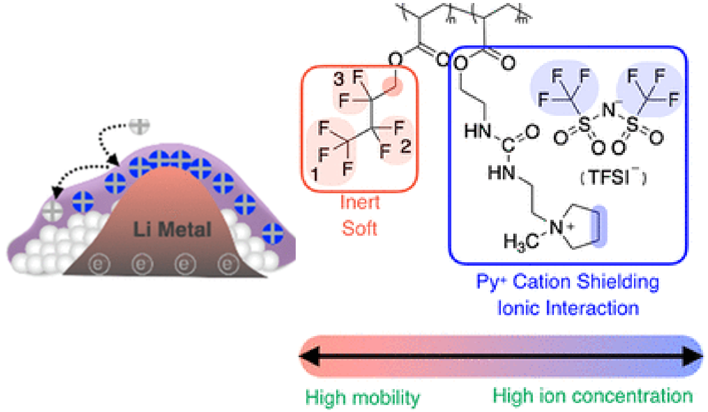
Effect of coating chemistry

Single-ion conductive flowable



Z. Yu, Y. Cui, Z. Bao et al., **Joule** 2019

Cation-tethered flowable



Z Huang+, S Choudhury+, H Gong, Y Cui, Z Bao, ***JACS***, 2020

Battery 500 publications

FY 20

1. D.T. Boyle, X. Kong, A. Pei, P.E. Rudnicki, F. Shi, W. Huang, Z. Bao, J. Qin, Y. Cui, "Transient Voltammetry with Ultramicroelectrodes Reveals the Electron Transfer Kinetics of Lithium Metal Anodes", **ACS Energy Lett**. 5, 701-709, 2020.

2. X. Kong, P. E. Rudnicki, S. Choudhury, Z. Bao, and Jian Qin, "Dendrite Suppression by a Polymer Coating: A Coarse-Grained Molecular Study", **Adv. Funct. Mater**., 1910138, 2020.

3. Z. Huang, S. Choudhury, H. Gong, Y. Cui, and Z. Bao " A Cation-Tethered Flowable Polymeric Interface for Enabling Stable Deposition of Metallic Lithium " **JACS** (2020) DOI: 10.1021/jacs.0c09649

4. C. V. Amanchukwu, Z. Yu, X. Kong, J. Qin, Y. Cui, and Z. Bao. "A new class of ionically conducting fluorinated ether electrolytes with high electrochemical stability." **Journal of the American Chemical Society** 142, 7393-7403, 2020.

5. Z. Yu, H. Wang, X. Kong, W. Huang, Y. Tsao, D.G. Mackanic, K. Wang, X. Wang, W. Huang, S. Choudhury, Y. Zheng, C. Amanchukwu, S.T. Hung, Y. Ma, E.G. Lomeli, J. Qin, Y. Cui, Z. Bao, "Molecular design for electrolyte solvents enabling energy-dense and long-cycling lithium metal batteries", **Nature Energy**, 5, 526-533, 2020.

6. Z. Yu, Y. Cui, Z. Bao, "Design principles of artificial solid electrolyte interphases for lithium-metal anodes", **Cell Rep. Phys. Sci.,** 1, 100119, 2020.

Battery 500 publications

FY 21

1. D.T. Boyle, W. Huang, H. Wang, Y. Li, H. Chen, Z. Yu, W. Zhang, Z. Bao, Y Cui, “Corrosion of lithium metal anodes during calendar ageing and its microscopic origins” **Nature Energy** 6, 5, pg 487-494, 35, 2021.

2. H. Wang, W. Huang, Z. Yu, W. Huang, R. Xu, Z. Zhang, Z. Bao, Y. Cui, “Efficient Lithium Metal Cycling over a Wide Range of Pressures from an Anion-Derived Solid-Electrolyte Interphase Framework” **ACS Energy Letters** 6, 2, pg 816-825, 14, 2021.

3. J. Li, Y. Cai, H. Wu, Z. Yu, X. Yan, Q. Zhang, T.Z. Gao, K. Liu, X. Jia, Z. Bao, “Polymers in Lithium-Ion and Lithium Metal Batteries” **Advanced Energy Materials** 11 (15), 2003239, 26, 2021.

4. S.C. Kim, X. Kong, R.A. Vilá, W. Huang, Y. Chen, D.T. Boyle, Z. Yu, H. Wang, Z. Bao, J. Qin, Y. Cui, “Potentiometric measurement to probe solvation energy and its correlation to lithium battery cyclability”, **Journal of the American Chemical Society** 143, 27, pg 10301-10308, 7, 2021.

5. H. Wang, Z. Yu, X. Kong, W. Huang, Z. Zhang, D.G. Mackanic, X. Huang, J. Qin, Z. Bao, Y. Cui, “Dual-Solvent Li-Ion Solvation Enables High-Performance Li-Metal Batteries”, **Advanced Materials**, 2008619, 17, 2021.

6. Y. Chen, Z. Yu, P. Rudnicki, H. Gong, Z. Huang, S.C. Kim, J.C. Lai, X. Kong, J. Qin, Y. Cui, Z. Bao, “Steric effect tuned ion solvation enabling stable cycling of high-voltage lithium metal battery”, **Journal of the American Chemical Society,** 143, 44, pg 18703-18713, 2, 2021.

7. Z. Huang, S. Choudhury, N. Paul, J.H. Thienenkamp, P. Lennartz, H. Gong, P. Müller-Buschbaum, G. Brunklaus, R. Gilles, Z. Bao, "Effects of Polymer Coating Mechanics at Solid-Electrolyte Interphase for Stabilizing Lithium Metal Anodes" **Advanced Energy Materials**, 2103187, 2021.

Battery 500 publications

FY 22

- Z.Yu, P.E. Rudnicki, Z. Zhang, Z. Huang, H. Celik, S.T. Oyakhire, Y. Chen, X. Kong, S. Kim, X. Xiao, H. Wang, Y. Zheng, G.A. Kamat, M. Kim, S.F. Bent, J. Qin, Y.Cui, Z.Bao, "Rational solvent molecule tuning for high-performance lithium metal battery electrolytes". **Nat Energy** 7, 94–106, 2022.
- M.S. Kim, Z. Zhang, P.E. Rudnicki, Z. Yu, J. Wang, H. Wang, S.T. Oyakhire, Y. Chen, S.C. Kim, W. Zhang, D.T. Boyle, X. Kong, R. Xu, Z. Huang, W. Huang, S.F. Bent, L. Wang, J. Qin, Z.Bao, Y.Cui, "Suspension electrolyte with modified Li^+ solvation environment for lithium metal batteries". **Nat. Mater.** 21, 445-454, 2022.
- H.Wang, Z.Yu, X. Kong, S. Kim, D.T. Boyle, J. Qin, Z. Bao, Y. Cui, Y., "Liquid electrolyte: The nexus of practical lithium metal batteries", **Joule**, 6, 588-616, 2022.
- Z. Zhang, Y. Li, R. Xu, W. Zhou, Y. Li, S.T. Oyakhire, Y. Wu, J. Xu, H. Wang, Z. Yu, D.T. Boyle, W. Huang, Y. Ye, H. Chen, J. Wan, Z. Bao, W. Chiu, Y. Cui, "Capturing the swelling of solid-electrolyte interphase in lithium metal batteries". **Science**, 375, 66-70, 2022.